



COMMONWEALTH OF VIRGINIA  
DEPARTMENT OF CONSERVATION  
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DIVISION OF MINERAL RESOURCES

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# GEOCHEMICAL RECONNAISSANCE FOR ZINC, LEAD, AND COPPER IN THE STAUNTON QUADRANGLE, VIRGINIA

RICHARD S. GOOD AND  
GARY C. ALLEN

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REPORT OF INVESTIGATIONS 31

VIRGINIA DIVISION OF MINERAL RESOURCES  
James L. Calver  
Commissioner of Mineral Resources and State Geologist

CHARLOTTESVILLE, VIRGINIA

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ERRATA Report of Investigations 31

Page 3, 4th paragraph, line 9: ...bath  
...should read...batch...

Page 4, last paragraph, lines 3-5: ...  
from the W-1 diabase standard  
used as soil standards, ...  
should read...were compared to  
W-1 diabase standard because  
soil standards...

Page 8, 1st paragraph, line 2: ...and  
each is above...should read  
...from each other at the...

Page 43, line 16: ... $y=0.3989e^{-x^2/2}$ ...  
should read... $y=0.3989e^{-x^2/2}$   
where  $x=0$  units for mean and  
area under curve=1...

# GEOCHEMICAL RECONNAISSANCE FOR ZINC, LEAD, AND COPPER IN THE STAUNTON QUADRANGLE, VIRGINIA

By

RICHARD S. GOOD AND GARY C. ALLEN <sup>1</sup>

## ABSTRACT

Atomic-absorption analyses were made on soils collected on a quarter-mile rectangular grid in the Staunton 7.5-minute topographic quadrangle. These were evaluated by comparison with quarter- and eighth-mile grids around known zinc mineralization in the nearby geologically similar Timberville area of the Shenandoah Valley. The areas of investigation are underlain by folded and fractured Upper Cambrian to Middle Ordovician sedimentary rocks, which are dominantly carbonates.

The data were evaluated by using histograms and probability curves for each geologic formation, and by using a floating mean ALGOL-trend surface program for the entire quadrangle. Soils overlying the Beekmantown Formation (Lower Ordovician) averaged 54 ppm and the distribution was markedly asymmetrical indicating an anomalous population. From probability curves, 180 ppm was determined as a threshold for reconnaissance sampling. Anomalous values were determined in an area north of Franks Mill in the northwestern part of the quadrangle, where sphalerite and fluorite are present on strike just outside the quadrangle. Weak anomalies of zinc and lead occur in other parts of the area. Copper can be used to delineate the presence of zinc and lead.

## INTRODUCTION

The purpose of the present investigation is to study the distribution patterns of zinc, lead, and copper in residual soils of the Staunton quadrangle, Virginia, and to provide a guide for further reconnaissance and detailed geochemical prospecting. A secondary purpose is to gather information on the relationship between bedrock and residual soils.

The Staunton 7.5-minute quadrangle is located in central Augusta County and is bounded by 79°00' and 79°07'30" west

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<sup>1</sup> Former staff member.

longitude and  $38^{\circ}07'30''$  and  $38^{\circ}15'$  north latitude (Figure 1). For comparison two known mineralized areas of similar geology

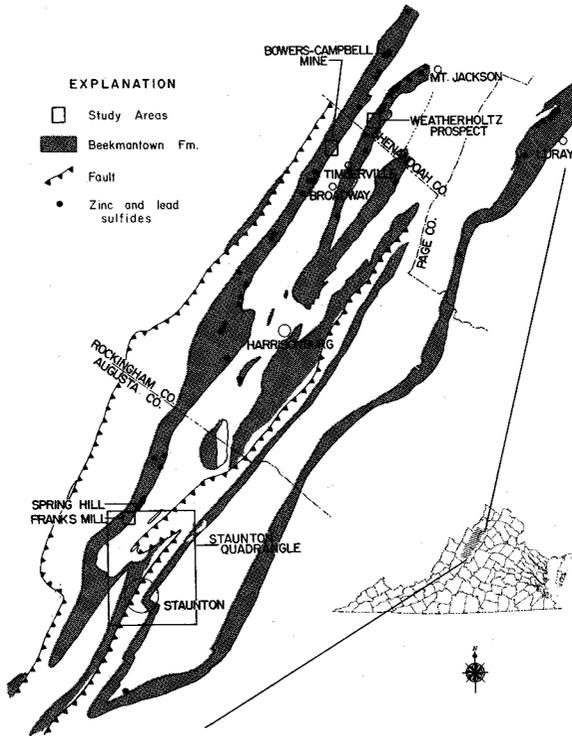


Figure 1. Index map showing location of Staunton quadrangle and zinc-lead occurrences in central Shenandoah Valley, Virginia (modified from Scherffius, 1969).

were studied: (1) in Rockingham County, the Bowers-Campbell Mine (Timberville Mine) in the 7.5-minute Timberville quadrangle ( $78^{\circ}45'$  to  $78^{\circ}52'30''$  west longitude and  $38^{\circ}37'30''$  to  $38^{\circ}45'$  north latitude) and (2) in Shenandoah County, the Weatherholtz prospect ("Timberville Mine") in the New Market 7.5-minute quadrangle ( $78^{\circ}37'30''$  to  $78^{\circ}45'$  west longitude and  $38^{\circ}37'30''$  to  $38^{\circ}45'$  north latitude).

The relationship of the areas studied to the regional occurrence of sulfides is shown in Figure 1. The Shenandoah Valley is part of the Valley and Ridge physiographic province. Discussions and illustrations of the regional geology of the area are in publications by Butts (1933, 1940-41), and on the Geologic Map of Vir-

ginia (Virginia Division of Mineral Resources, 1963). A detailed geologic map of the Staunton quadrangle was prepared by Rader (1967) and the surface geology of the Bowers-Campbell Mine is described by Stephenson (1949). Geology around the Weatherholtz prospect is included in Thornton's (1953) study of the Mt. Jackson 15-minute quadrangle and the geology of Rockingham County was done by Brent (1960). Characteristics of sulfide mineralization are discussed by Herbert and Young (1956) and Scherffius (1969).

The authors would like to acknowledge the cooperation and assistance of Dr. James L. Calver, Commissioner of Mineral Resources and State Geologist, who encouraged the study. Charles Pearson assisted in the field and laboratory work, and Oliver Fordham assisted in some of the laboratory and computer work.

## PROCEDURES

### Sample Preparation

At each sample site a hole was dug to a depth of 1.6 feet and the bottom was cleaned to remove surface contamination. A fist-sized sample was removed from the wall, at 1.5 feet and placed in a cloth bag. The samples were air dried and any rock chips in the soil samples were removed. The soil was ground to -100 mesh in an agate mortar and stored in polystyrene vials.

Ground sample material, weighing 0.500 gram, was placed in 100 ml teflon beakers and dissolved in 45 ml of a concentrated 1:2 nitric-hydrofluoric acid mixture and 2 ml perchloric acid. Excess acid was driven off by heating the sample to dryness. The residue was dissolved in 1 ml hydrochloric acid and the solution was diluted to 50 ml, yielding a concentration of 10,000 parts per million of sample in solution. The solutions were stored in polyethylene bottles for atomic-absorption analysis. A reagent blank was prepared for each bath of samples.

### Atomic Absorption

All samples were analysed on a Techtron Model AA-4 atomic absorption spectrophotometer, using Westinghouse multi-element hollow cathode lamps: Pb-Zn-Ag and Fe-Cu-Mn. Low response on the most sensitive absorbing line for lead, 2170 Å, necessitated use of the less sensitive 2833 Å line. Drift was corrected by re-

peaking. An acetylene-air flame with an air pressure of 20 psi and a gas flow of 2.5 liters per minute was used. Instrumental operating parameters are given in Table 1.

Table 1.—Instrumental operating parameters for atomic absorption analyses.

<i>Element</i>	$\overset{\circ}{\text{A}}$ <i>Wave Length</i>	<i>Lamp</i> <i>Current</i>	<i>Na</i> <i>Slit</i>	<i>Limit of</i> <i>Detection</i> <i>ppm</i>
Cu	3247, 3273	10	25	0.03
Zn	2139	8	300	0.02
Pb	2833	8	300	0.2

Elemental concentrations were registered on a Photovolt Vari-cord 43 log-linear recorder. The relative peak heights were then compared to standard zinc, copper, and lead curves that were made at the beginning, middle, and end of each run.

#### Accuracy and Reproducibility

Analytical techniques were checked by running 11 subsamples of a soil overlying the Beekmantown Formation in the Staunton quadrangle, by running 11 subsamples of a trace-metal standard (W-1, standard diabase), and by the method of standard additions to 17 soil-sample solutions of different concentrations. The technique was further checked for possible interelemental interference and light scatter from calcium, magnesium, aluminum, potassium, sodium, barium, and iron by preparing "synthetic soil solutions" corresponding to the normal range of major elements in the soil and adding, or spiking, the solution with known amounts of trace metals. Special purity standards were used for this purpose (Johnson and Matthey Company, Ltd., London, England).

Accuracy was determined from comparison of a rock standard with the most acceptable value of a number of laboratories (Figure 2). Trace element values from the W-1 diabase standard, used as soil standards, were not available at the time of laboratory investigation. The zinc value determined from 11 subsamples of W-1 in this study is 88 ppm which compares favorably with other laboratories using atomic absorption. The most acceptable zinc value is 82 ppm (Fleischer, 1969). Similarly, the W-1 value for copper was 126 ppm and this compares favorably in magnitude with 110 ppm (Fleischer, 1969). Only comparative-

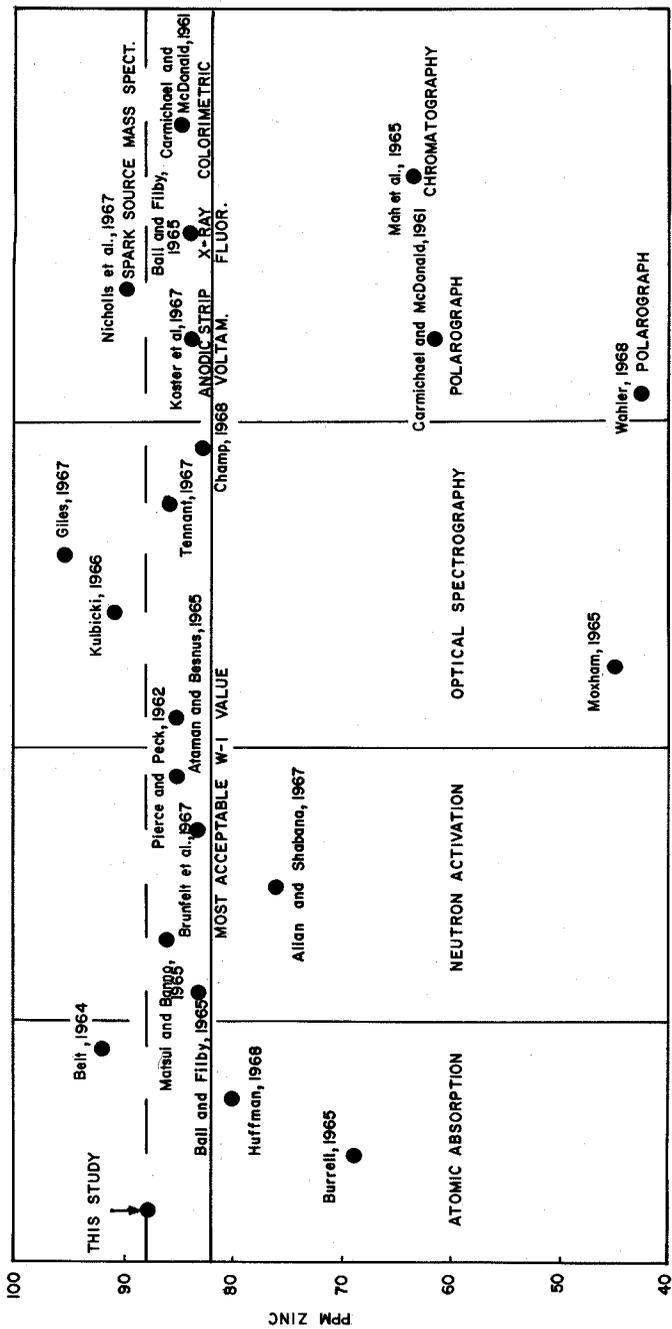


Figure 2. Interlaboratory variability in W-1 zinc (data from Fleischer, 1969).

ly high lead values of those in this report are included in the section on "geochemical anomalies," because lower lead values are subject to error due to light scatter.

Reproducibility of instrumental variation was checked by taking 11 subsamples of a dried soil and running each of these five times (Table 2). The arithmetic means for these subsamples were averaged and the reproducibility of subsample variation was determined (Table 3).

Table 2.—Reproducibility of instrumental values for zinc.

Analyst, R. S. Good

<i>Subsample</i>	<i>Range of five runs ppm</i>	<i>Arithmetic Mean ppm</i>	<i>Standard Deviation ppm</i>	<i>Relative Standard Deviation</i>
1	151-157	154	2.97	1.93
2	173-184	176	2.41	1.37
3	147-151	148	1.57	1.06
4	154-162	159	3.58	2.26
5	154-160	156	2.77	1.78
6	143-150	146	2.52	1.73
7	147-150	150	2.68	1.79
8	146-150	148	1.46	0.99
9	160-168	163	3.74	2.29
10	170-179	175	4.03	2.31
11	159-166	163	2.95	1.81

Table 3.—Reproducibility of soil subsample values for zinc.

<i>Subsample Range ppm</i>	<i>Arithmetic Mean ppm</i>	<i>Standard Deviation ppm</i>	<i>Relative Standard Deviation</i>
146-179	158	10.4	6.61

### Use of Trace Element Histograms

Histograms or bar charts are the simplest way of showing the distribution of a trace element population in soil. A trace element population is a function of its subpopulations, such as grain size, mineralogy, and other characteristics. For example, it is generally known that sandstones tend to have lower zinc values and shales higher zinc values than carbonate rocks (Turekian and Wedepohl, 1961). Generally, soils having abundant clay and iron-oxide content have high zinc values (White, 1957). Residual soils over unmineralized bedrock thus usually consist of largely overlapping trace element subpopulations, each with slightly

different arithmetic means. As a result these subpopulations tend to produce an asymmetric or skewed histogram. For example, Figure 3 represents the asymmetric distribution for all 863 samples in the Staunton quadrangle.

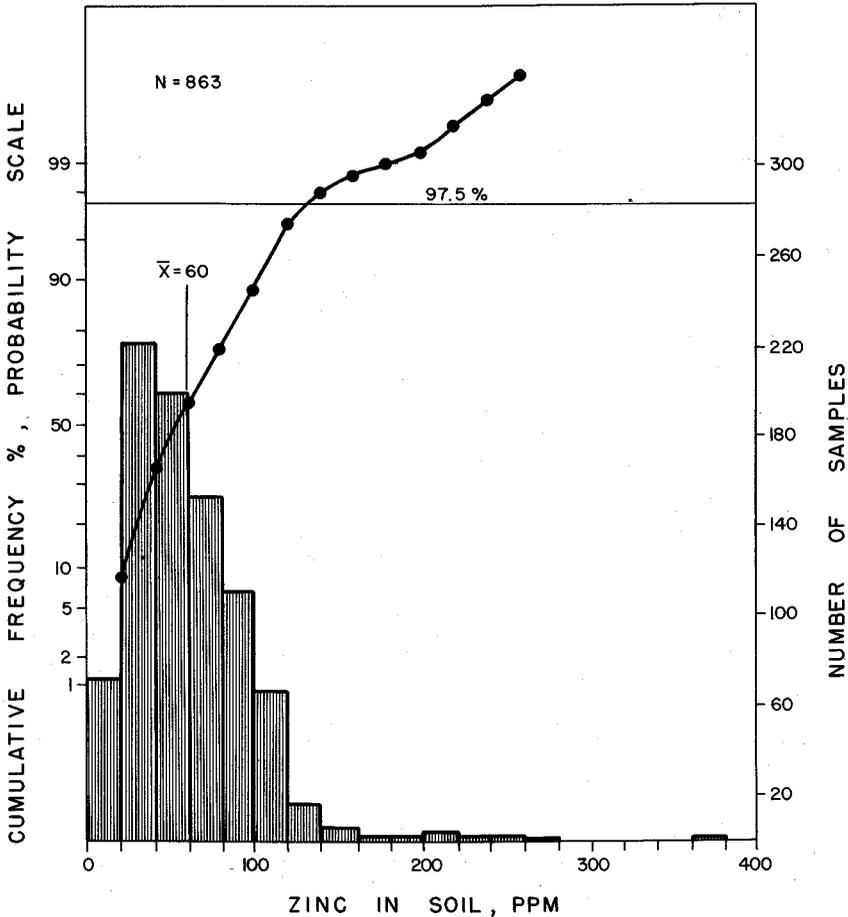


Figure 3. Histogram and probability plot of zinc for 863 quarter-mile soil samples, Staunton quadrangle.

Histograms for zinc in soils developed on different geologic formations in the Staunton quadrangle are shown in Figure 4. The arithmetic mean for 863 samples collected on a 0.25-mile grid is 60 ppm. The highest mean, 87 ppm, is over the Martinsburg Formation and the lowest, 40 ppm, is over the Conoco-

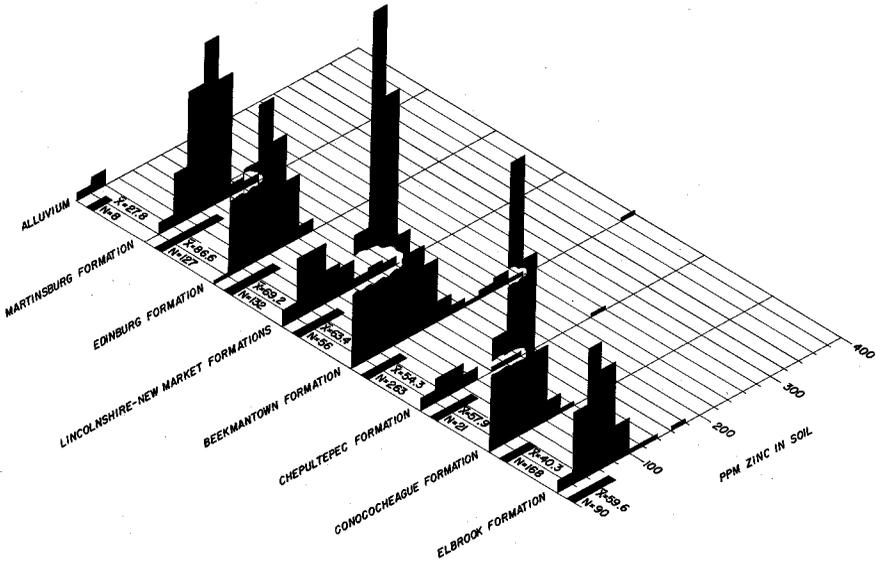


Figure 4. Histograms of zinc in soils for each geologic formation.

cheague Formation. These two means are significantly different and each is above 99 percent confidence level. Some of the zinc histograms that are categorized by geologic formation approach a symmetrical distribution like the Martinsburg and Conococheague formations, and others are markedly asymmetric such as the Beekmantown, Lincolnshire, and New Market formations.

In a trace element population of soils which include some samples over mineralized bedrock, the difference between the mineralized and unmineralized subpopulations is usually large enough to show some high values over mineralized rock strung out in a tail or slight second "hump" that indicates a distinct anomalous population even when the background population is asymmetric. Figure 5 is a histogram model with a sufficient number of anomalous samples (100) to clearly show the overlapping second population (modified after Hawkes and Webb, 1962 from Tennant and White, 1959). This data is also plotted on a cumulative percent frequency probability scale. The bend in the curve clearly indicates the break between the two populations, both of which approach a normal curve, or a straight line on a probability plot if graphed separately. If the sampling density is increased a larger number of samples over the mineralized rock are included and the second anomalous population becomes more apparent.

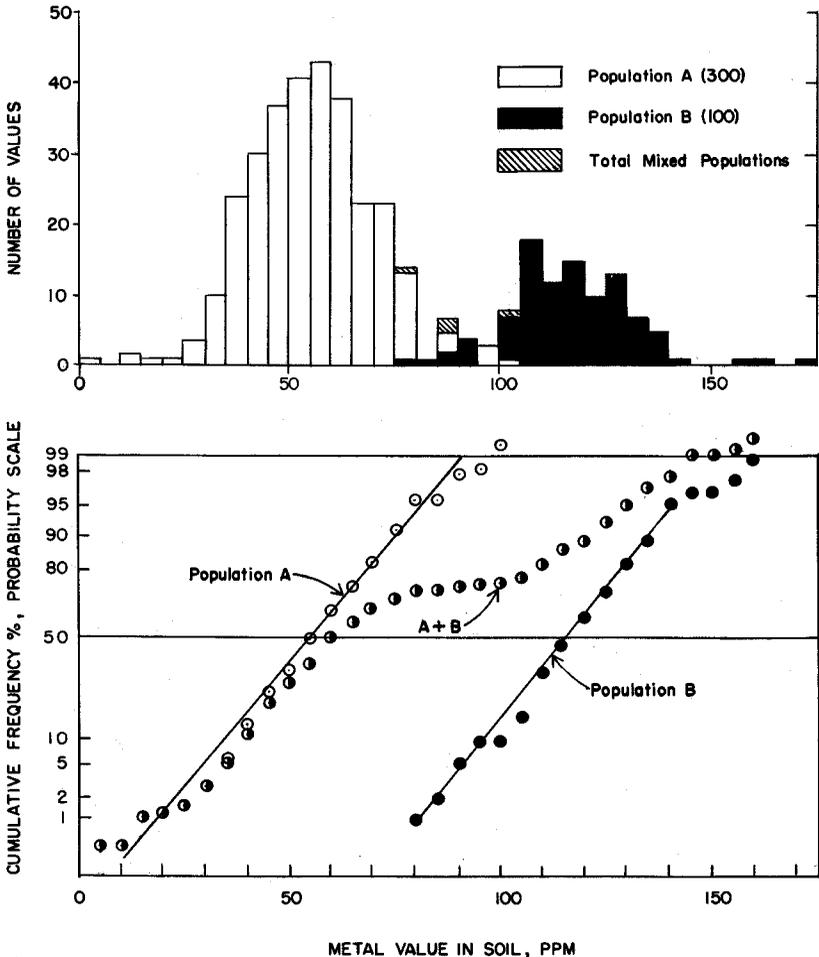


Figure 5. Model of background and anomalous population resolved in probability plot (modified after Hawkes and Webb, 1962).

Figure 6 contains a cumulative probability curve for zinc for 263 quarter-mile spaced samples over the Beekmantown Formation of the Staunton quadrangle. This plot is superimposed on the standard histogram. It can be seen that if values greater than 97.5 percent are used they correspond to a distinct break in the probability curve and two populations are clearly suggested. By reading the corresponding zinc value, 180 ppm for the 97.5 per-

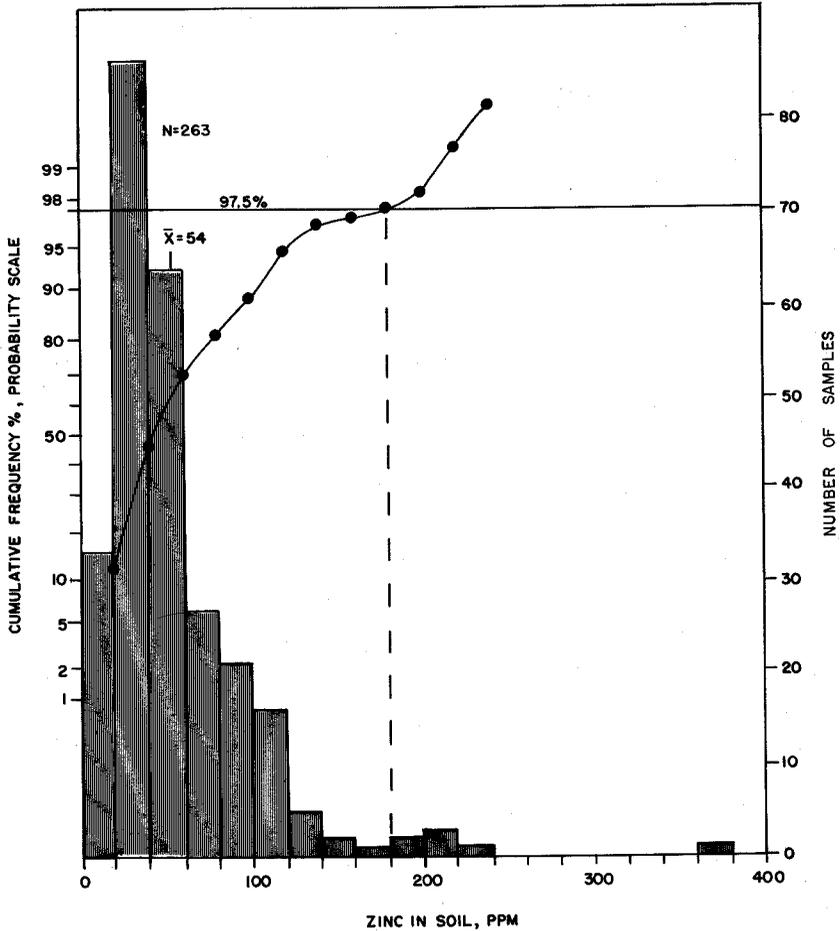


Figure 6. Histograms and probability plot for zinc in soil over the Beekmantown Formation.

cent line, a threshold value is suggested. This value was further checked by comparison with known mineralized areas, the Bowers-Campbell Mine and the Weatherholtz prospect, and found to be similar.

Figure 7 depicts a cumulative probability curve for zinc for 127 samples over the Martinsburg Formation. The curve is almost a straight line suggesting a nearly symmetric distribution and no second or anomalous population. It is very likely that here the values above 97.5 percent are not related to mineralization or

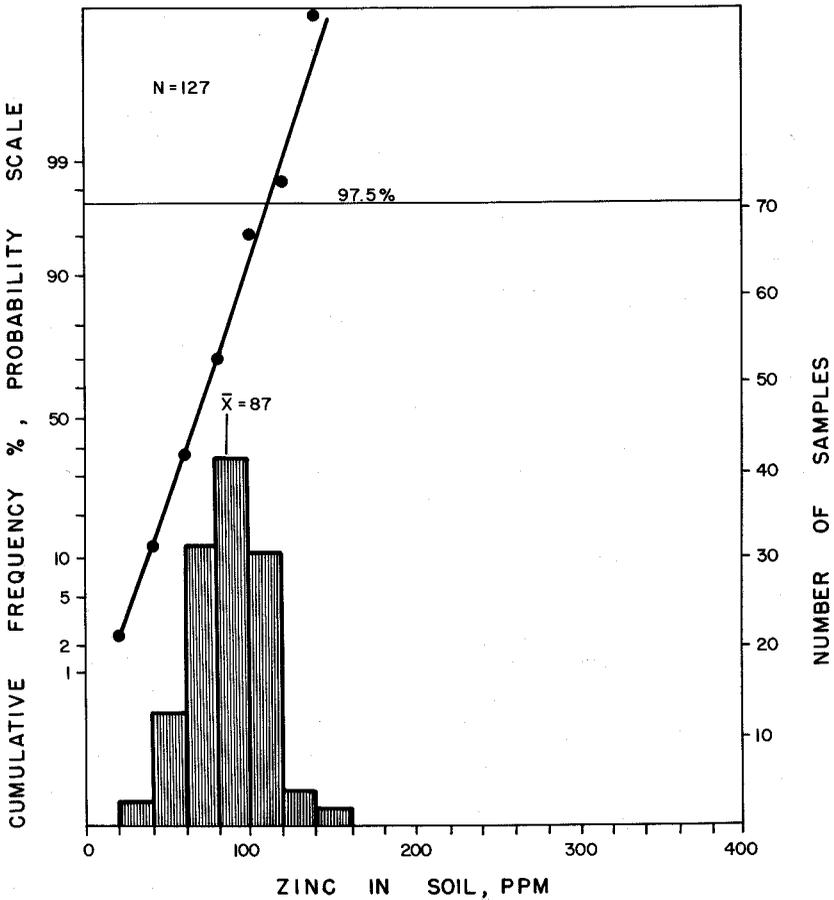


Figure 7. Histogram and probability plot for zinc in soil over the Martinsburg Formation.

a second anomalous population since the curve is symmetric and there are no scattered high values.

The distribution of lead by geologic formation is shown in Figure 8. Though lead data should only be used as a guide, it can be seen from the lead histograms that the Beekmantown Formation is the only formation with more than a few values above 100 ppm (the Martinsburg, Edinburg, and Elbrook have none). No cumulative probability curves were constructed because of the relatively poor analytical accuracy of lead, but 100 ppm was adopted as a rough guide to threshold by inspection of the histo-

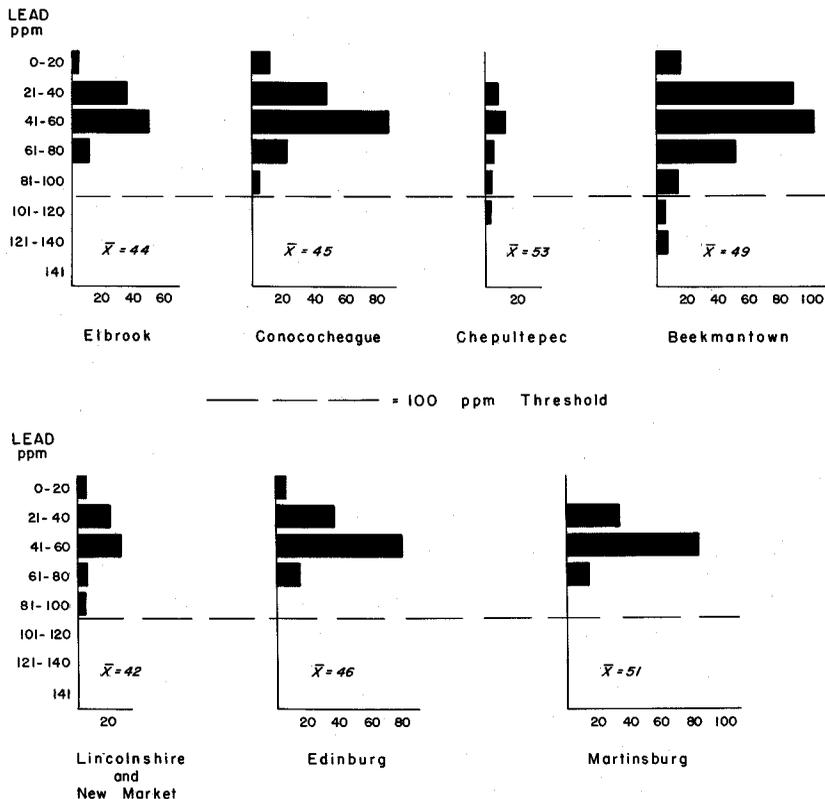


Figure 8. Histograms of lead in soils for each geologic formation.

grams. This value appeared to be useful when compared with known mineralization around the Bowers-Campbell Mine and the Weatherholtz prospect (Figure 15). Only 5 values above 100 ppm, in a northeastern trend that passes through the vicinity of the Bowers-Campbell shaft, are evident in a one-square mile block of 76 soil samples around the mine. Only one value above 100 ppm, near the shaft area, was shown in 81 samples in a square mile around the Weatherholtz prospect.

The distribution of copper in several geologic formations is shown in Figure 9. The means ranged from 22 ppm for the Chepultepec to 38 ppm for the Martinsburg with an intermediate value of 24 ppm for the Beekmantown. The histograms for most formations are asymmetrical, particularly for the Beekmantown and to a lesser degree for the Martinsburg. It appeared that some copper values were associated with zinc in and around

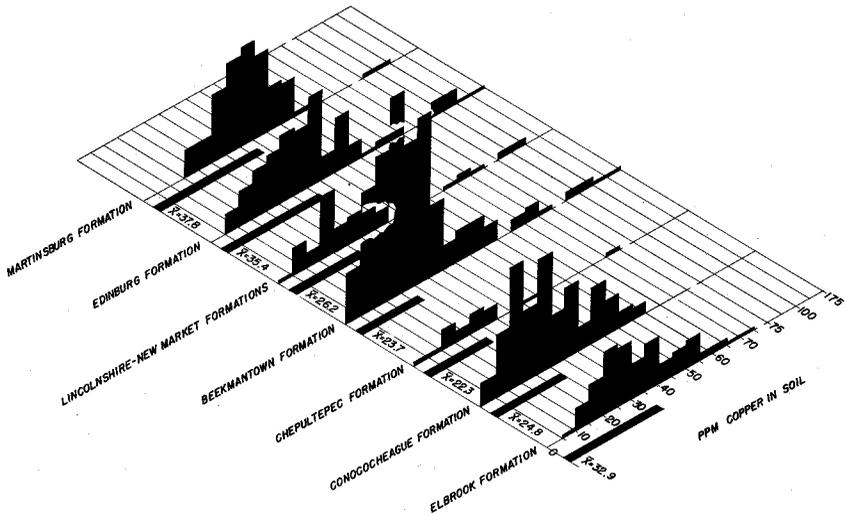


Figure 9. Histograms of copper in soil for each geologic formation.

known mineralized areas. Because copper is geochemically more mobile and thus more widely dispersed than zinc or lead in the soil, the presence of slightly higher than background copper values in the soil may be helpful in delineating the shape of a zinc anomaly or indicate the presence of the less mobile zinc or lead. However, the selection of the "threshold" for a trace element that is only a minor "pathfinder" element and does not reflect significant copper sulfide mineralization was more difficult. A copper threshold of 55 ppm was finally decided by inspection of the histograms and consideration of values around the mineralized areas.

### GEOLOGIC SETTING

The Staunton quadrangle is locally characterized by gently sloping limestone and dolomite hills 50-150 feet high; a few cherty, conical hills 200-400 feet high; low, narrow, sandy, limestone ridges, 150-200 feet high; and steep limestone and dolomite cliffs 100-300 feet high along some of the incised meanders of the Middle River. Level areas are limited to alluvial bottom lands along the Middle River. There is very gentle relief in areas underlain by shale. The minimum elevation is 1200 feet above sea level and the maximum is 1940 feet; the total relief is 740 feet.

The Upper Cambrian to Middle Ordovician limestones, dolomites, cherty limestones and dolomites, shales, and thin sand-

stones are briefly described in Table 4. With the exception of a few, less than 50-feet wide, poorly exposed alkalic and diabasic

Table 4.—Geologic formations in the Staunton quadrangle, Virginia (after Rader, 1967).

Age	Unit	Character	Approximate thickness in feet
Quaternary	Alluvium	Sand and clay.	50-160
	Quarter-nary (?)	Terrace gravel	
Cretaceous-Jurassic	Alkalic intrusive rocks	Dikes and plugs of alkalic composition.	
Triassic	Diabase intrusive rocks	Diabase dikes.	
Ordovician	Martinsburg Formation	Buff to gray, calcareous, silty shale; some greenish sandstone.	2000+
	Edinburg Formation	Dense, black, argillaceous limestone; black shale and dark-gray, nodular-weathering limestone.	1200
	Lincolnshire Formation	Medium-grained, dark-gray, cherty limestone.	75-225
	New Market Limestone	Dove-gray, compact, high-calcium limestone.	0-200
	Beekmantown Formation	Thick-bedded, light-gray, fine-grained dolomite; some medium-gray limestone; abundant chert.	1800-2000
	Chepultepec Formation	Dark-gray to black limestone; some thin beds of dolomite; nodular black chert.	300-400
Cambrian	Conococheague Formation	Laminated gray limestone, thick-bedded dolomite, and thin sandstone beds.	2200-2500
	Elbrook Formation	Thin to thick-bedded limestone and dolomite, shaly dolomite.	2000+

dike rocks, there are no outcrops of igneous or metamorphic rocks in the quadrangle.

The Cambrian and Ordovician sedimentary rocks (Figure 10) of the Staunton area have been folded along northeasterly-southwesterly axes. The major fold structures from northwest to southeast are: the Long Glade syncline, Middlebrook anticline, and Massanutten synclinorium.

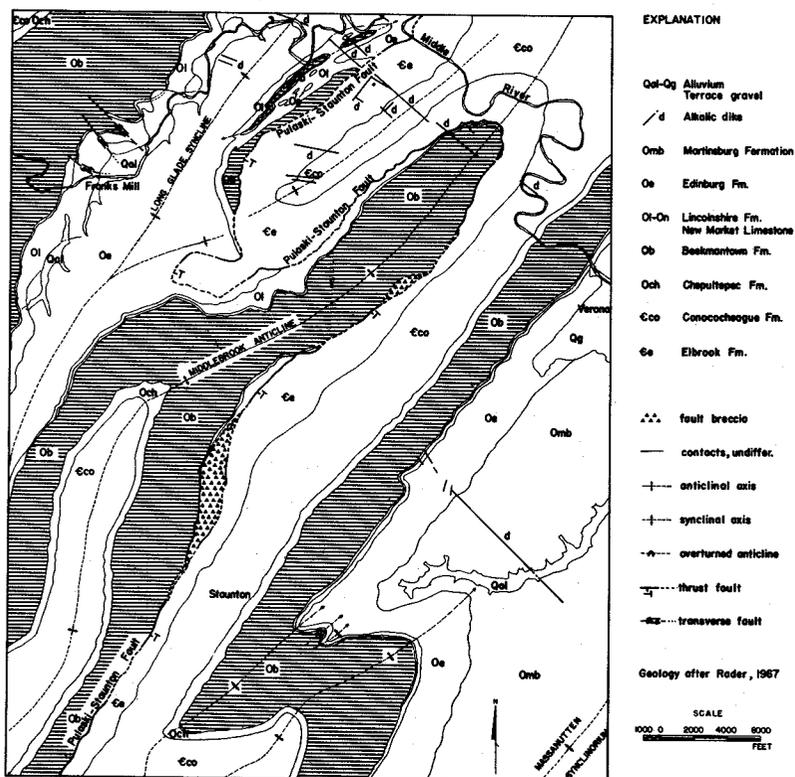


Figure 10. Geology of Staunton quadrangle (after Rader, 1967).

A major zone of broken strata is found along the Pulaski-Staunton fault which has a northeasterly-southwesterly trend. In most places the Elbrook Formation has been thrust to the northwest over the Beekmantown Formation. The fault has been

folded with the development of the Middlebrook anticline; large masses of breccia and "crush conglomerate" have been formed and the largest mass is more than 2 miles long by a quarter-mile wide. Small areas of breccia are associated with the noses of folds and the collapse material in caves.

### SOILS

The soils of the Staunton quadrangle are principally residual loams and silts. The soil over formations having abundant chert content is rocky in character, particularly on hills within the Beekmantown Formation; it is sandy in character over the low, calcareous sandstone ridges of the Conococheague Formation. Alluvial sand and gravel is largely limited to terraces and bottom lands along the Middle River and Lewis Creek.

Unless the soil has been partially removed by erosion there is commonly developed a soil change at a depth of 8-12 inches marking the break between a zone of leaching (A horizon) and a zone of partial precipitation and accumulation (B horizon). The loams and silts are dominantly light gray or pale yellow to brown in the A horizon and red to brown in the B horizon. Over sandstones and cherts, the A horizon soil is generally lighter in color than that over carbonate rocks and may be gray or pale yellow to yellow orange. The color of the soil depends principally on the amount of iron and its oxidation state, the clay content, and organic material. In the area studied, the light gray to grayish-brown soils have a low zinc and iron content. Those in areas of anomalous zinc content tend to be reddish brown to dark brown.

Leaching in the A horizon has partially removed potassium, sodium, calcium, magnesium, iron, aluminum, and manganese, thus leaving residual enrichment of silica. This horizon frequently contains microscopic, euhedral quartz with authigenic overgrowths. Any appreciable calcium in the A horizon is related to the presence of fragments of undecomposed carbonate rocks. The B horizon is characterized by increased clay content (kaolinite, halloysite, montmorillonite, and/or illite) and iron oxides (limonite, goethite, and/or hematite). It is known that zinc (White, 1957) is associated largely with the clays, particularly montmorillonite, and the iron oxides.

Although major element distribution in the soil is strongly influenced by leaching, the trace elements zinc, copper, and lead do not appear to be markedly affected in residual soils over un-

mineralized or "background" areas. (Table 5) A vertical profile, however, taken 50 feet from the leveled dumps of the Bowers-

Table 5.—Vertical soil profiles.

<i>Background</i>		<i>Beekmantown Formation</i>			
Feet	ppm Zn	<i>50' from Bowers-Campbell dump</i>			
		ppm Zn	ppm Cu		
0.25	—	1350	33		
0.5	51	79	37		
1.0	51	97	45		
1.5	48	147	60		
2.0	50	198	67		
2.5	54	287	85		
Ox	2.2				
V	4.5				

<i>Elbrook Formation</i>		<i>Edinburg Formation</i>			
Feet	ppm Zn	Feet	ppm Zn	Feet	ppm Zn
0.5	37	0.5	49	0.5	108
1.0	35	1.0	68	1.0	105
1.5	45	1.5	78	1.5	104
2.0	40	2.0	83	2.0	112
2.5	bedrock	2.5	66	2.5	97
Ox	3.5		12.7		5.6
V	9.0		18.4		8.8

Campbell Mine has a top layer of zinc-rich washed fines on top of residual, clayey soil over the Beekmantown Formation thus indicating both contamination and increasing zinc content with

Table 6.—Horizontal variability around anomalous soil station 4-31 (Figure 25) Franks Mill area, Staunton quadrangle; Beekmantown Formation, 1.5 feet deep.

	Zn ppm	Cu ppm	Pb ppm	Fe %	Al <sub>2</sub> O <sub>3</sub> %	Quartz Index	Color
10'W	73	17	78	1.3	8.8	83	buff
C	41	12	37	1.5	4.9	89	light brown
10'E	42	14	35	1.0	3.7	62	light brown
100'N	89	16	74	1.4	7.7	72	light brown
100'NE	39	10	47	1.7	6.5	79	light gray
100'E	34	10	43	1.8	5.6	104	light gray
100'SE	300	73	122	3.5	16.1	33	reddish brown
100'S	183	59	106	2.6	11.3	84	reddish brown
100'SW	67	12	59	1.5	3.3	84	light brown
100'W	86	21	61	1.3	8.4	100	light brown
100'NW	69	21	55	1.3	8.6	64	light brown

depth. Erratic trace element values in anomalous areas vary horizontally as well. Table 6 shows the horizontal variability of 11 samples around one station in the northwestern part of the Staunton quadrangle. Soil samples were taken 10 feet west and 10 feet east of the station and eight samples were taken at compass points 100 feet from the center. This data shows that in the upper B horizon a surface anomaly can be very local, and sharply delineated. Similarly, an example of a horizontal profile between two stations, a quarter-mile apart, on the Beekmantown Formation is shown in Table 7.

Table 7.—Horizontal variability in zinc in soil between two background stations in Beekmantown Formation.

Feet North	ppm Zn
0	86
100	54
200	75
300	61
400	64
500	94
600	52
700	59
800	98
900	47
1000	88
1100	66
1200	123
1320	61

$$\bar{X} = 71$$

$$\% CV = \pm 30$$

Original sample stations a quarter-mile apart showed 50 and 63 ppm zinc.

Common types of geochemical trace metal soil anomalies in humid, non-glaciated areas are shown in Figure 11. It is clear from the foregoing discussion that reconnaissance-type sampling has limitations such as dilution by soil creep, displaced mineralization, or masking by deep soil cover. Nevertheless, weak individual values may be significant. In order to establish a trace metal threshold, a statistical approach may be applied and additional information about each lithologic unit or geologic formation be incorporated in an evaluation.

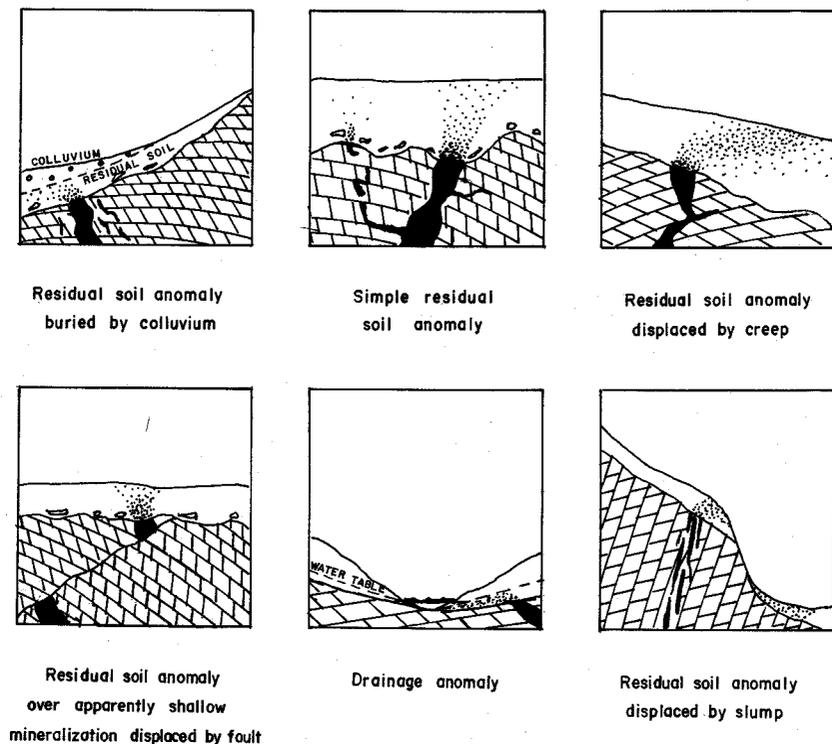


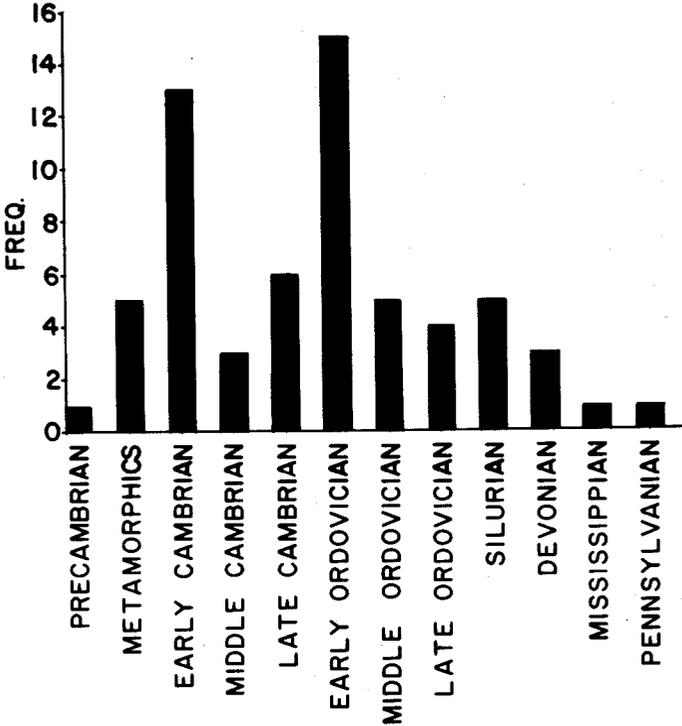
Figure 11. Common types of geochemical soil anomalies in humid, non-glaciated areas (modified after Hawkes and Webb, 1962).

## GEOCHEMICAL ANOMALIES

An area of known zinc-lead occurrences is more than one hundred miles in length. Of the almost 60 locations most are in the Beekmantown Formation (Herbert and Young, 1956; Scherffius, 1969). The belt of known sulfide occurrences was extended further southwest in Augusta County with the discovery in 1972 of sphalerite in Lower Devonian carbonates along the Calfpasture River. Sphalerite and fluorite occur west of Spring Hill and extend into the Franks Mill area (personal communication, Young, 1971) in the northwestern part of the Staunton quadrangle. Although it would appear that in the central Shenandoah Valley there is an almost exclusive preference of zinc-lead mineralization for the Beekmantown Formation (Figure 1), an examination of Wedow, Heyl, and Sweeney's (1968) compilation of 66 occurrences in the Appalachian region shows that zinc-lead sulfides occur in Paleozoic rock from early Cambrian to Pennsyl-

AGE OF HOST ROCK FOR 66 APPALACHIAN

ZINC-LEAD OCCURRENCES



HOST ROCK LITHOLOGY

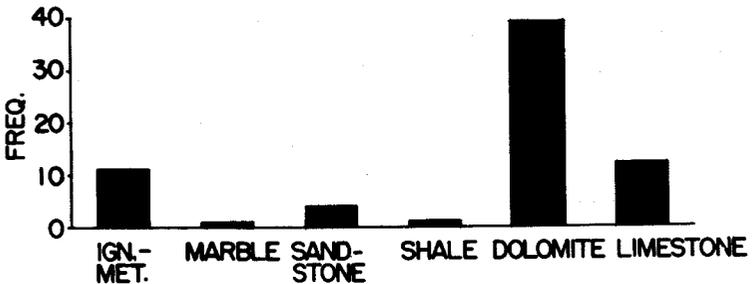


Figure 12. Frequency of lithology and geologic age for 66 of the most important known Appalachian zinc-lead occurrences (compiled from Wedow, Heyl, and Sweeney, 1968).

vanian age and in sandstones and shales as well as carbonates (Figure 12).

### Bowers-Campbell Mine

The Bowers-Campbell Mine (Figures 13 and 14), located 1.9 miles northwest of Timberville, Rockingham County, was operated for sphalerite from 1957-1962 by Tri-State Corporation and is now worked for agricultural lime by the Timberville Lime Company. The ore is in a boot-shaped, nearly vertical, sphaleritic-breccia body in upper Beekmantown dolomite. The only ore mineral is sphalerite and it is accompanied by small amounts of

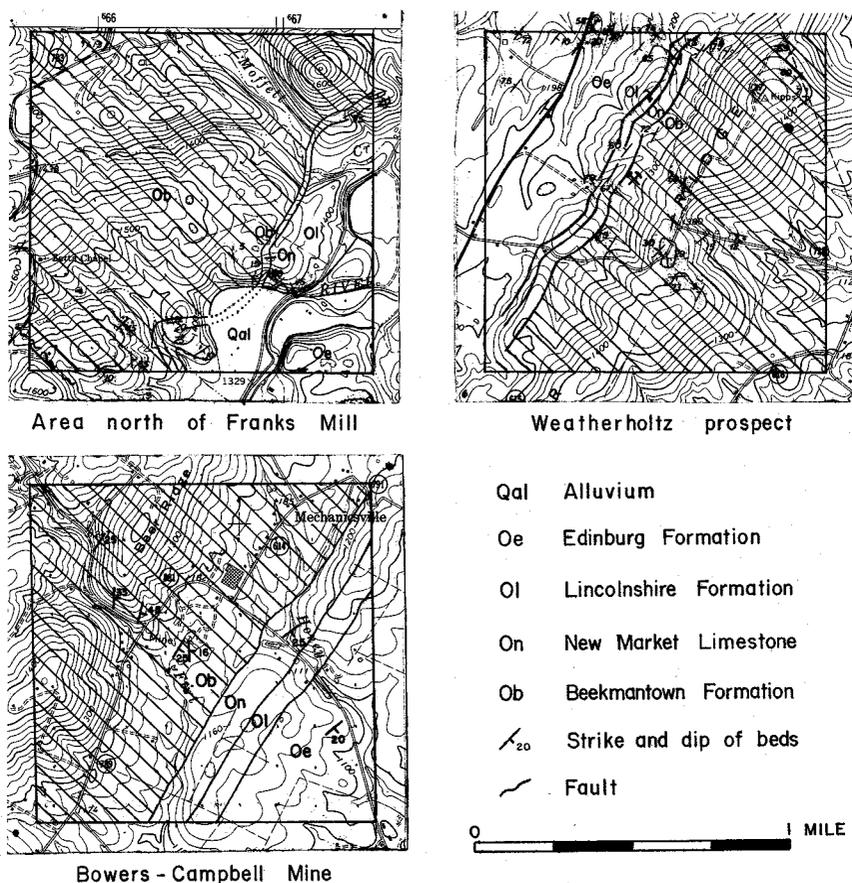


Figure 13. Surface geology of area north of Franks Mill and in the Bowers-Campbell Mine and Weatherholtz prospect areas.

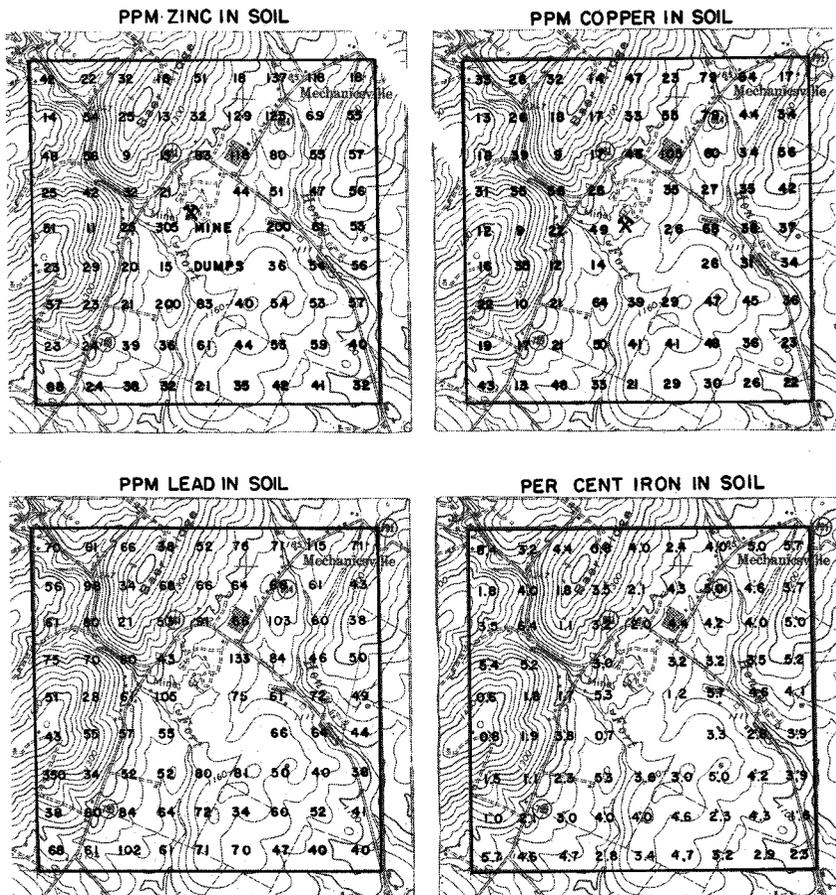


Figure 14. Zinc, copper, lead, and iron values in the soil for a one-square mile area around the Bowers-Campbell Mine, Rockingham County.

galena, chalcopyrite, pyrite, greenockite, smithsonite, and fluo-rite; gangue minerals are dolomite, quartz, and calcite. The areal geology shown in Figure 13 is modified from Stephenson (1949) and Brent (1960).

Soil sampling (Figure 15) was done in a one-square mile area at eighth-mile intervals with a total of 76 samples collected; none were taken from mine dumps. Three samples were found to have values greater than the threshold (180 ppm zinc) for soils over the Beekmantown in the Staunton quadrangle (Figure 6). None of the three samples are very high: 200, 200, and 305 ppm zinc, but all were taken adjacent to the mine area. The lack of any broad anomaly around the Bowers-Campbell can be explained

by the fact that the ore body cropped out over an area of a few square feet, and plunged steeply to the southwest (Herbert and Young, 1956; Hayes, 1960).

A simplified anomaly plot based on probability curves of zinc and copper (Figure 15) shows a weak copper high around the mine area, particularly to the northeast. The copper values also

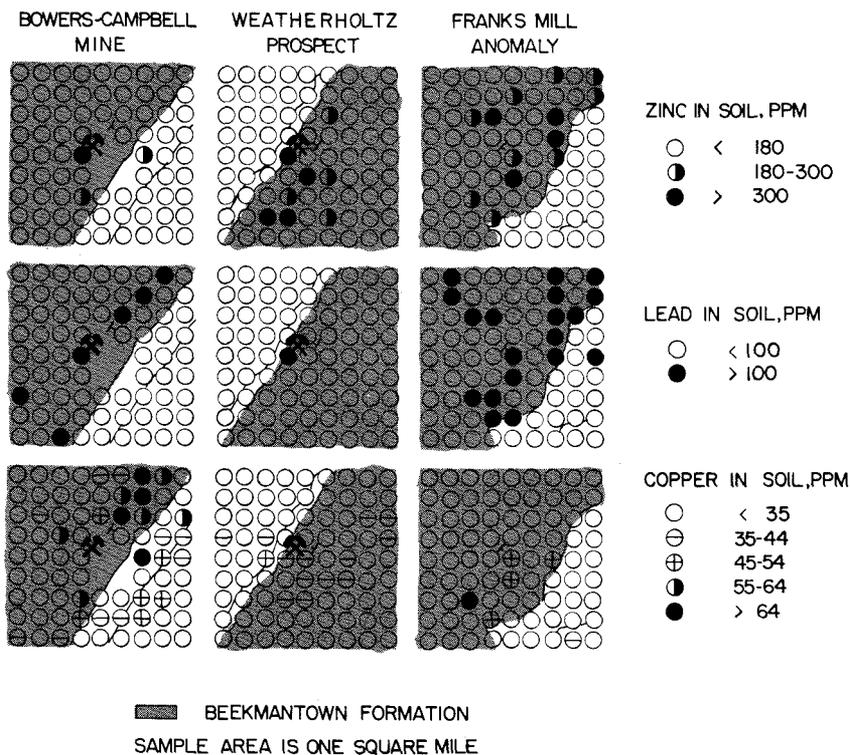


Figure 15. Anomalous zinc, lead, and copper values in one-square mile areas around Bowers-Campbell Mine, Weatherholtz prospect, and Franks Mill area.

correspond to subanomalous but higher zinc values and this relationship is reflected in a significant correlation coefficient (see Glossary) of  $+0.69$  (Figure 16). The small amount of chalcopyrite which occurs with the sphalerite ore would appear to be helpful as a prospecting guide because of the higher mobility in a carbonate soil environment of copper compared to lead or zinc.

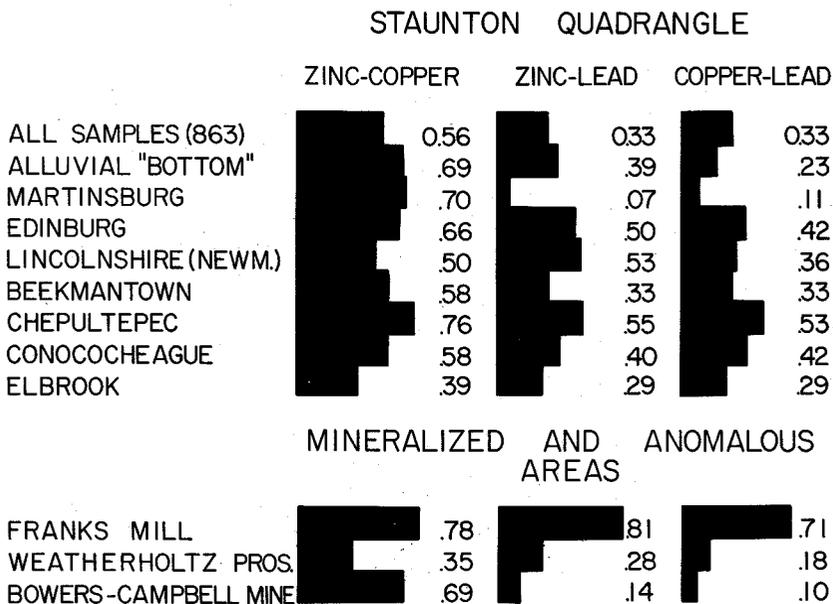


Figure 16. Trace-metal correlations in the Staunton quadrangle by geologic formation compared to mineralized and anomalous areas.

Histograms of zinc and copper are given in Figures 17 and 18 respectively.

Galena (lead sulfide) occurs sporadically in the Bowers-Campbell Mine near the edges of the breccia, but never in commercial amounts. Lead has no significant linear correlation with zinc (+0.14), copper (+0.10) or iron (+0.05); such values are close to a random relationship. However, six soil sample values having greater than 100 ppm Pb, the highest 350, form a northeasterly-southwesterly trend.

Although the iron values have moderate correlation with zinc (+0.46) and copper (+0.58), there appears to be no obvious pattern; iron is of limited value in searching for ore bodies with little or no gossan similar to the Bowers-Campbell Mine (Figure 19). In a strip one mile wide and about 8.6 miles long over the entire western edge of the Staunton quadrangle, 131 samples indicated that iron has apparently significant correlations with copper (+0.73), zinc (+0.59), and lead (+0.71) suggesting that these trace metals probably follow variations of the montmorillonitic-rich clay and hydrous iron-oxide content of the B

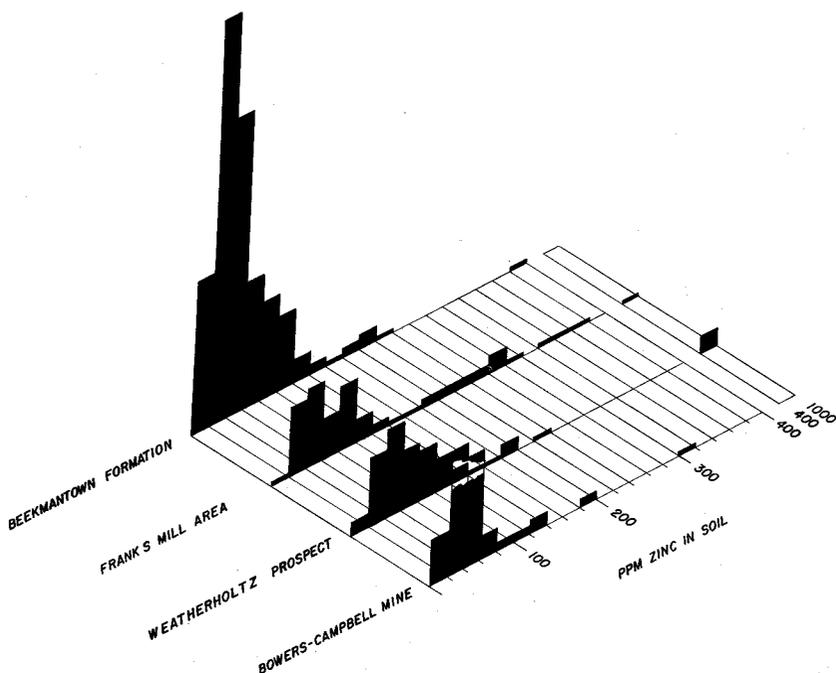


Figure 17. Histograms of zinc in soil in one-square mile around the Bowers-Campbell Mine, Weatherholtz prospect, and Franks Mill area compared to Beekmantown Formation, Staunton quadrangle.

horizon soils without any special indication of geochemical anomalies.

### Weatherholtz Prospect

The shaft of the Weatherholtz prospect, which is filled in with rubble and soil, is located on the western slope of Timber Ridge in Shenandoah County 0.6 mile east-northeast of the junction of State Road 728 and State Highway 42 and about 4 miles north of Timberville. The areal geology shown in Figure 13 is modified from Thornton (1953). The mineralogy is similar to that of the Bowers-Campbell Mine: brownish-yellow to greenish-brown sphalerite and pyrite with vein dolomite, quartz, calcite, barite, and gypsum. Traces of greenockite have also been reported (Herbert and Young, 1956; Scherffius, 1969).

An 80-foot inclined shaft with cross cuts was constructed (U. S. Bureau of Mines, 1949) and sphalerite was found, but in insufficient tonnage for commercial operation. Oxidization at the

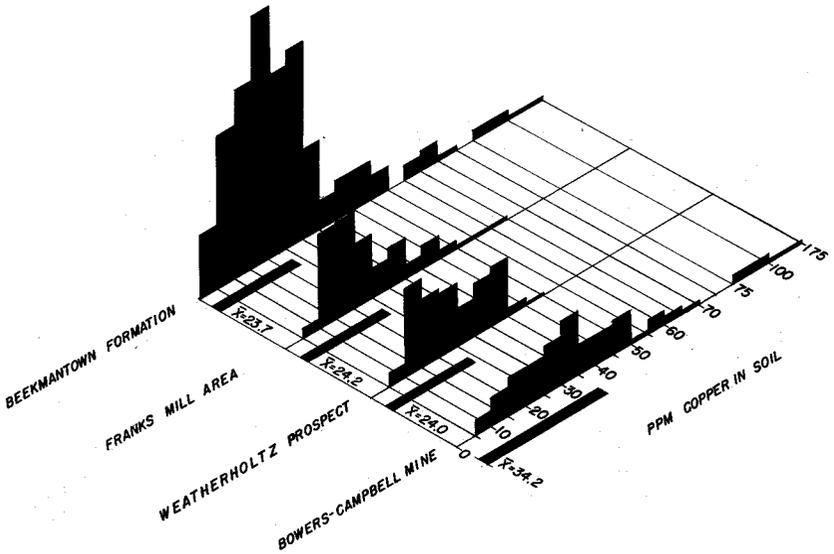


Figure 18. Histograms of copper in soil in one-square mile around the Bowers-Campbell Mine, Weatherholtz prospect, and Franks Mill area compared to Beekmantown Formation, Staunton quadrangle.

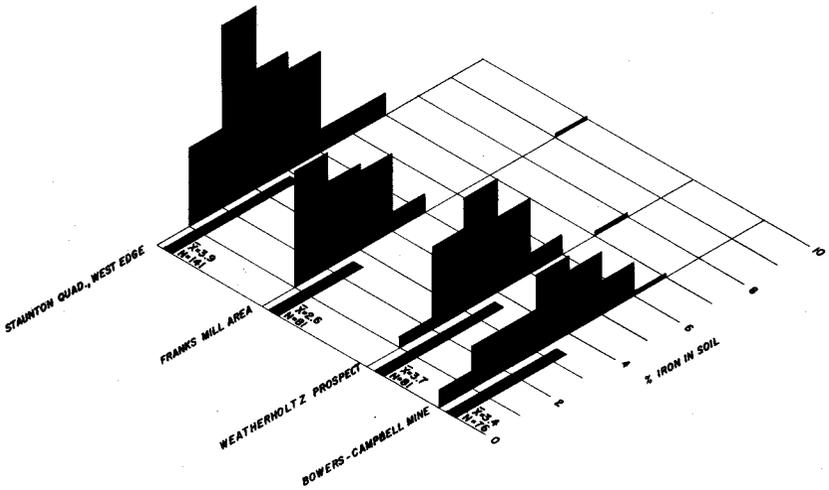


Figure 19. Histograms for total percent iron around the Bowers-Campbell Mine, Weatherholtz prospect, Franks Mill area, and western edge of Staunton quadrangle.

shaft was observed to a depth of 6 feet. At 42 feet a one-foot-wide vein had an assay of 11.24 percent zinc and at the bottom a vein 2.2 feet wide assayed 12.9 percent.

Soil sampling in a one-quarter mile area (81 samples, eighth-mile intervals) around the Weatherholtz shaft (Figures 15 and 20) showed eight values above 180 ppm zinc in soils over the

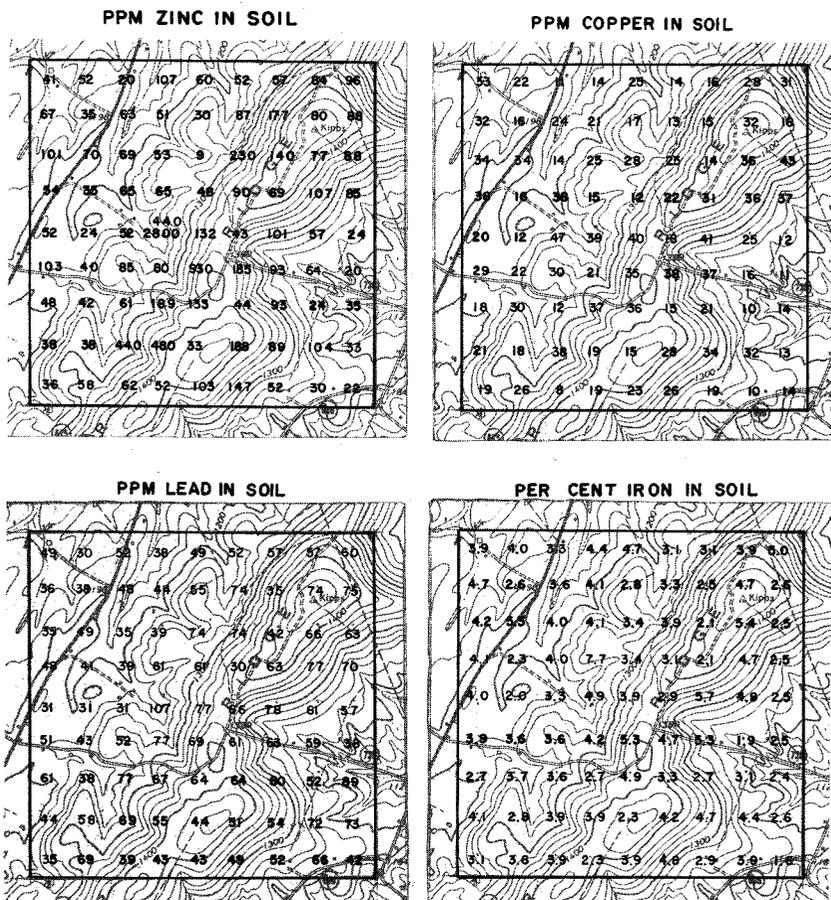


Figure 20. Zinc, copper, lead, and iron values in the soil, Weatherholtz prospect, Shenandoah County; area is one-square mile.

northeastward-trending upper Beekmantown. This anomaly was higher than around the Bowers-Campbell Mine and four values were greater than 400 ppm zinc, the highest being 2800 ppm, a value that may result from spurious concentration in the im-

mediate vicinity of the shaft. There is very little visible waste material near the shaft. Copper values have a northeasterly trend and a minor northwesterly cross trend. The copper-zinc correlation coefficient from the Weatherholtz prospect was markedly lower (+0.35) than at the Bowers-Campbell Mine (+0.69) (Figure 16). Only one value greater than 64 ppm copper, near the shaft, could be considered anomalous on a cumulative probability curve.

Only one anomalous lead value (107 ppm) was determined from a sample collected near the shaft; the lead-zinc correlation coefficient was very weak (+0.28). Aluminum, iron, and barium were also analyzed in each sample. The only significant coefficients were the positive relationships between aluminum and copper (+0.65) and iron and aluminum (+0.59). Barium appears to be associated with the aluminum in clays (+0.41) but not with zinc. The iron values above 4.5 percent iron reflected northeasterly and northwesterly cross trends corresponding with weak copper and zinc highs.

#### Staunton Quadrangle

All reconnaissance stations established on a quarter-mile grid in the Staunton quadrangle are illustrated in Figure 21. Anomalous stations for zinc, lead, and copper are indicated with large circles and are based on cumulative probability curves for each formation within the quadrangle compared to trace metal values around the two mineralized areas just discussed. All zinc anomalies greater than 180 ppm and lead values greater than 100 ppm are within or close to the outcrop of the Beekmantown Formation. Copper anomalies greater than 55 ppm are generally outside the Beekmantown, although six coincide with zinc anomalies in it. There is a lead-copper anomaly in soils over the Chepultepec Formation northwest of Staunton (Figure 21, location C). Further to the northeast (Figure 21, location G), a north-westward-trending, weak copper anomaly appears to be present in the Beekmantown Formation. Other weak anomalies are a zinc-copper anomaly at near the east-central city limits of Staunton (Figure 21, location F) and a zinc-copper anomaly west of the city limits (Figure 21, location D).

*Franks Mill Area:* In the northwestern portion of the Staunton quadrangle (Figure 21, location A) there are four zinc values over 180 ppm, the highest 378 ppm. A one-square-mile area was

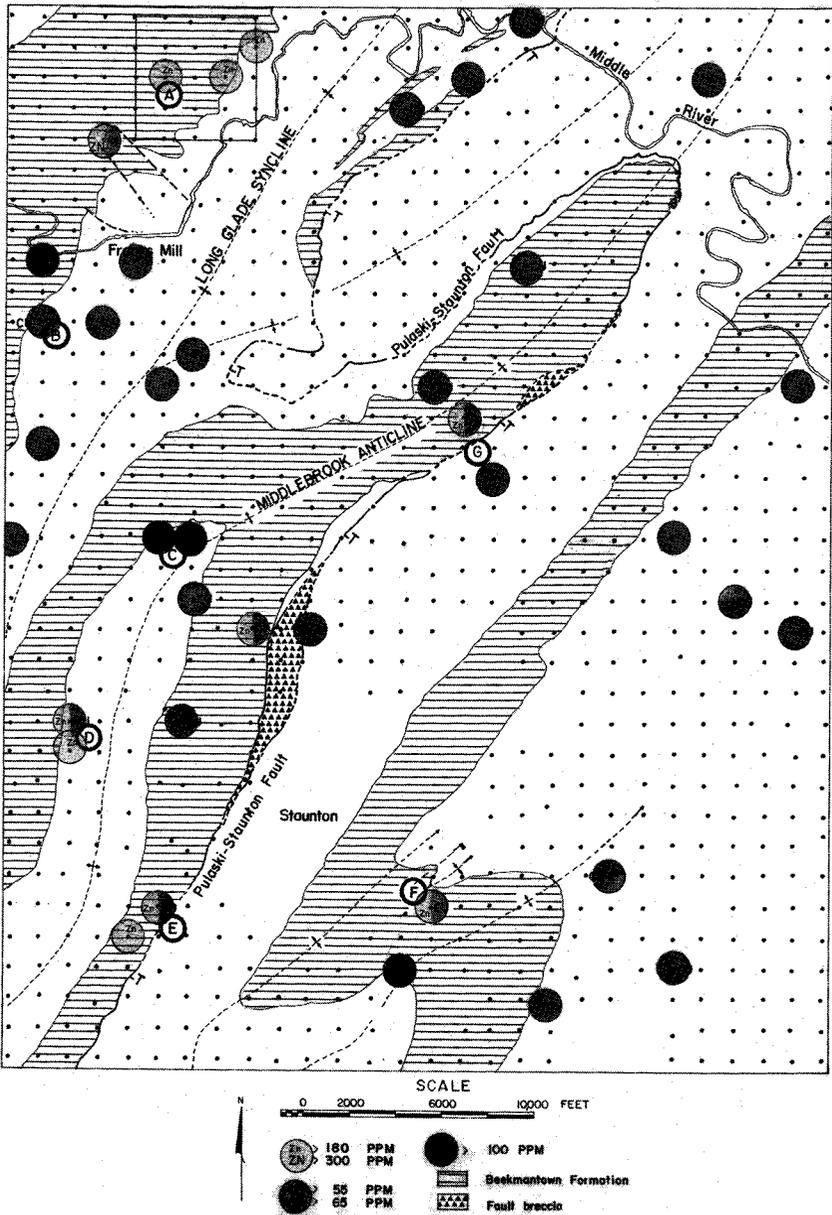


Figure 21. Trace-metal anomalies on a quarter-mile grid, Staunton quadrangle.

chosen north of Franks Mill (Figures 15 and 22) for further examination and 81 samples were taken at eighth-mile intervals.

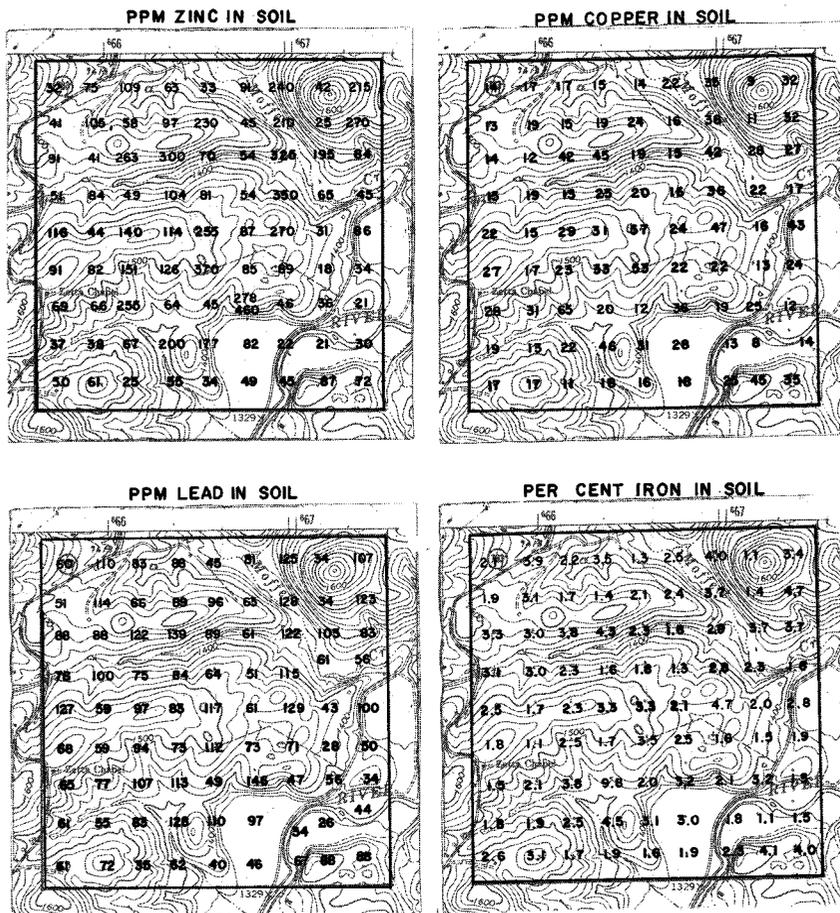


Figure 22. Zinc, copper, lead, and iron values in the soil in a one-square-mile block north of Franks Mill, Staunton quadrangle.

This area is on strike with reported sphalerite-fluorite showings west of Spring Hill (Young, 1967). There were fifteen values for zinc above the 180 ppm level, the highest, 460 ppm. This is comparable in a favorable way to the sample areas around the Bowers-Campbell Mine (three anomalous values, the highest 305 ppm) and the Weatherholtz prospect (seven anomalous values, the highest, 930 ppm) (Figure 17). Copper and zinc showed a correlation coefficient of  $+0.78$  at Franks Mill compared to  $+0.69$  at Bowers-Campbell Mine.

Lead values were scattered with no obvious pattern, but 20 out of 81 were greater than 100 ppm compared to six in the Bowers-

Campbell Mine and only one in the Weatherholtz prospect. The correlation coefficient for zinc and lead was high (+0.81). Most of the high lead values (19 out of 20) were in soils over upper Beekmantown rocks.

Within the Franks Mill vicinity the zinc trends are northeasterly-southwesterly, following the strike of the Beekmantown. Rader (1967) has shown three parallel northwestward-trending cross faults just southwest of the area and the topography along Moffetts Creek reflects the possibility of additional faults being present. Small areas of breccia and recrystalline dolomite were observed along the hillside northeast of Moffetts Run but no sulfides other than pyrite were seen.

### ALGOL TREND-SURFACE PROGRAM

Computer-derived regional trend surfaces are, by now, fairly well documented in the literature. Krumbein (1959), Harbaugh (1963), Nordeng, Ensign, and Volin (1964), Conner and Miesch (1964), and Nackowski, Mardirosian, and Botbol (1967), pioneered in computer derived trend surfaces. More recently, Botbol (1971), Cameron and Hobbs (1971), and Nairis (1971), among others, have applied trend surfaces to mining exploration. Recent critical evaluations of the technique have come from Howarth (1967), Chayes (1970), Doveton and Parsely (1970), and Baird, Baird, and Morton (1971). The present program is a translation by Gary C. Allen of a BALGOL program by Harbaugh (1963) to ALGOL using a Burroughs 5500 computer.

Trend surfaces in geochemical prospecting are described by arithmetic equations that define surfaces which tend to fit the raw trace-element values on a three-dimensional plot so that scatter is averaged out in a way similar to the familiar "best fit" or least-squares curve used on two-dimensionally graphed data. Thus, in a three-dimensional plot the first degree or linear equation would be a plane tilted up toward the area with most trace-element highs. A second degree or quadratic equation would be a curved surface tending to fit the individual points more closely. Higher order equations would progressively come closer and closer to fitting all the points exactly; if such were the case, the original purpose would be defeated because an unnecessarily complex equation requiring an inordinate amount of computer time would be used to make what a simple, direct, contouring program could generate. What is desired is a second- or third-

order equation which smooths out analytical and sampling background scatter, but is responsive to changes in background lithology, thus providing a "floating background mean". This technique eliminates the necessity of knowing the geology or the distribution histograms by lithologic unit. The floating mean surface is shown in computer printout as 10 ppm contours delineated by symbols alternating with blank areas. In this manner only broad highs and lows are shown and individual one- or two-station anomalies will not greatly affect the shape of the contours.

Figures 23 and 24 show quadratic (2nd order) and cubic (3rd order) printouts for zinc in the Staunton quadrangle. There is very little difference between the two levels of equations. The cubic trend shows high background in the northwest and south-

ZINC: GEOCHEMICAL RECONNAISSANCE MAP, STAUNTON, VA., QUADRANGLE, C1=J0

.....  
 CONTOURS OF LINEAR+QUADRATIC TREND SURFACE

X VALUE LEFT EDGE OF MAP = 0.1 X VALUE RIGHT EDGE OF MAP = 2.6 Y VALUE TOP EDGE OF MAP = 0.1  
 Y VALUE BOTTOM EDGE OF MAP = 3.5 REFERENCE CONTOUR VALUE = 100.0 CONTOUR INTERVAL = 10.0



Figure 23. ALGOL quadratic printout for zinc, Staunton quadrangle. Values represent parts per million for contouring.

east corners. The southeast corner is underlain by Martinsburg shale with the highest (87) arithmetic mean of all the formations of the quadrangle but no known zinc mineralization. The other high is in the northwest corner in an area of zinc anomalies and known mineralization. One of the limitations of trend-surface

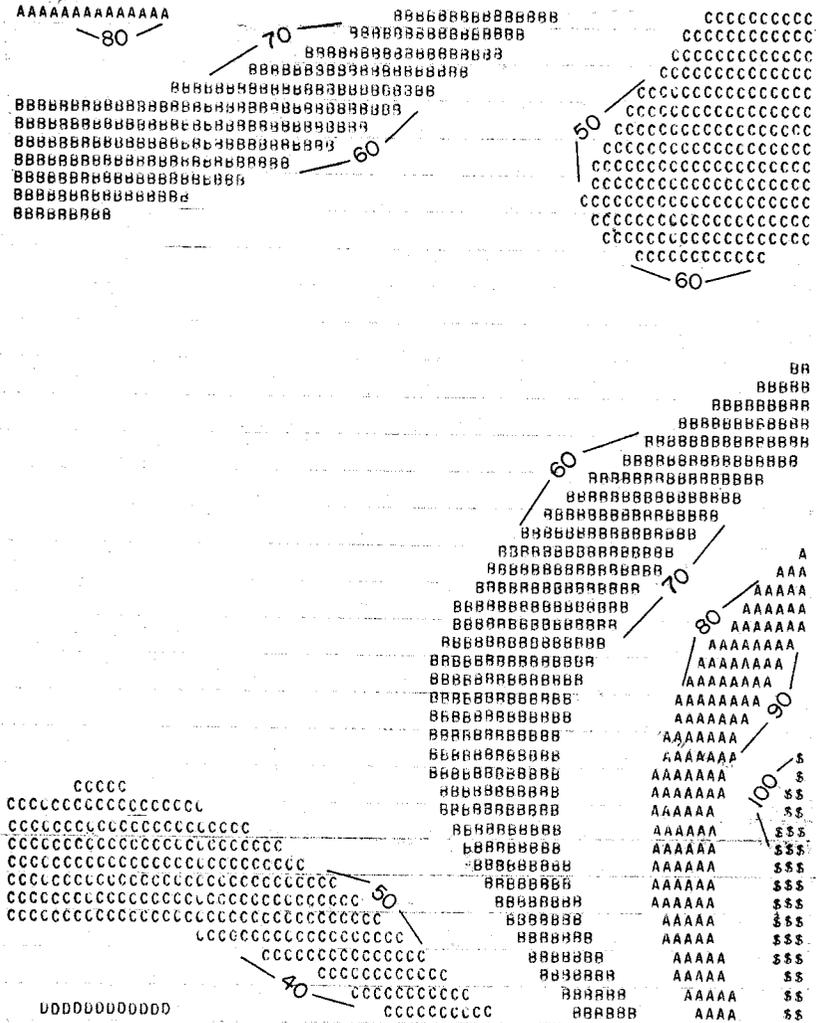


Figure 24. ALGOL cubic printout for zinc, Staunton quadrangle. Values represent parts per million for contouring.

techniques is the distortion produced at edges and particularly at corners because the computer tends to continue the surface either up or down according to the last corner values. This problem can be corrected by sampling several rows outside the area of investigation.

The most useful aspect of the trend surfaces is the delineation of the residual values. These values are the difference between the measured station value and the cubic trend surface (Figure 24). The residuals can either be positive or negative. Figure 25 shows areas with positive residuals above the cubic trend surface or floating mean and individual stations with values of 2 and 2.5 standard deviations above the floating mean. These anomalous stations are all in or close to the Beekmantown Formation. With one exception these stations are in positive residual areas. The areas of most interest for further study are indicated in Figure 25 where there are two or more anomalous (solid black circles, 2.5 standard deviation) stations.

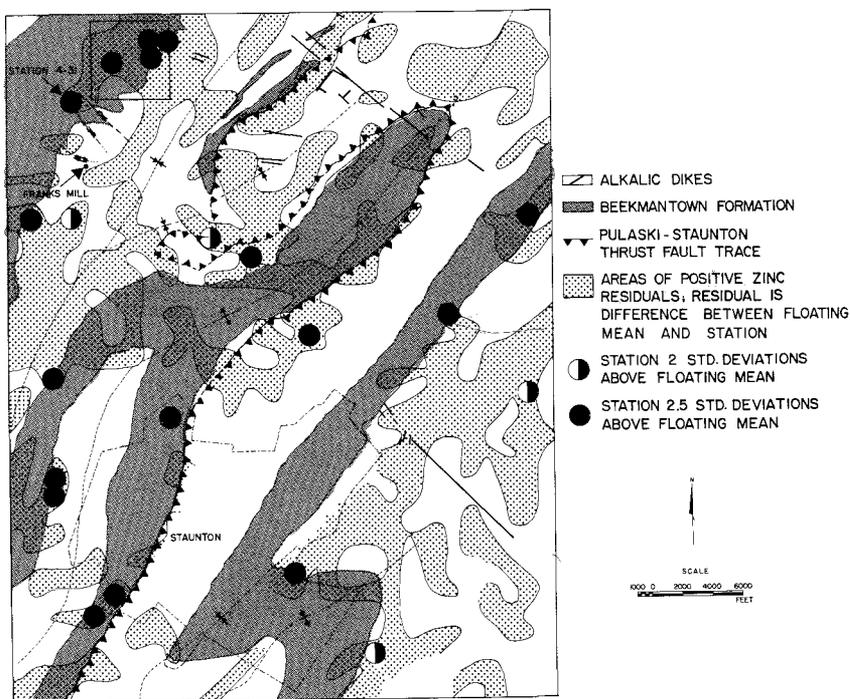


Figure 25. Positive zinc residuals from cubic trend-surface and anomalous stations, Staunton quadrangle.

## SUMMARY

1. Analytical precision by atomic absorption was sufficient to provide abundance values for zinc and copper in upper B horizon residual soils of the Staunton quadrangle by geologic formation. Lead values may be used as a guide only.
2. Background averages for zinc have statistically significant differences (at 95 percent or greater confidence levels) by geologic formation.
3. The probability curve for 263 Beekmantown Formation samples has a distinct break at 97.5 percent of the data corresponding to 180 ppm zinc. This value was found to be a useful threshold when applied to two known mineralized areas outside the quadrangle, both in Beekmantown rocks. The probability plot for zinc in all formations (863 samples) has an almost identically shaped curve and threshold value. Thresholds were established for copper (55 ppm) and lead (100 ppm).
4. Zinc and copper correlation coefficients range between 0.4-0.7 in both background and anomalous areas. Copper is useful in delineating zinc-lead anomalies because it is more widely dispersed than zinc or lead.
5. Vertical distribution of zinc in soils over unmineralized bedrock showed little fluctuation at depths to 2.5 feet, but over mineralized bedrock there were marked fluctuations with depth.
6. Reconnaissance sampling at quarter-mile intervals in the Staunton quadrangle revealed several low-level zinc and lead anomalies which merit further investigation. The highest zinc value, 378 ppm, was found in the northwestern portion of the quadrangle, north of Franks Mill. Resampling of a square mile on an eighth-mile interval showed 15 samples out of 81 with more than 180 ppm, the highest, 460 ppm. At the same interval, the Franks Mill area compares favorably with one-square-mile sample blocks around two mineralized areas, the Bowers-Campbell Mine and the Weatherholtz prospect. Bowers-Campbell, exclusive of ore-dump areas, showed only three values above 180 ppm zinc, the highest 305 ppm. The Weatherholtz prospect showed five values out of 81, the highest 930 ppm.

7. Trend surface residuals from computerized treatment of the zinc data at the quadratic or cubic level have usefulness for smoothing out background scatter and indicating deviations above the floating mean. Trend-surface data using cubic equations reflect the same anomalous stations as the probability technique. These stations were almost entirely within or close to Beekmantown outcrops and within broad areas of positive trend-surface residuals. Trend-surface techniques are useful, particularly in areas without detailed geologic maps, because of the independence of trend surfaces of background variation with lithology.

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## GLOSSARY

**arithmetic mean**—The sum of all the values divided by the total number of values.

**background** — The normal range in abundance of an element in soils over bedrock barren of ore. The range may vary because of soil composition, rock type, and geographic area.

**background average** — Same as arithmetic mean.

**confidence level** — The number of chances in a hundred (probability) that a given value falls within a certain range which is not due to chance. Most commonly the 95 percent level is used to indicate statistical significance.

**confidence limits** — Ninety-five percent of data lies between 1.96 (commonly, 2) standard deviations above and below the arithmetic mean. Also a 95 percent confidence limit represents values that are reliable 95 out of a 100 times.

**correlation coefficient** (also Pearson moment or linear correlation) — A measure of the dependence of one trace element value on the value of another trace element.

$$r = \frac{\sum(X-\bar{X})(Y-\bar{Y})}{\sqrt{\sum(X-\bar{X})^2 \sum(Y-\bar{Y})^2}} = \frac{\sum(X-\bar{X})(Y-\bar{Y})}{\sqrt{N-1} \sigma_x \sigma_y}$$

$r$  = correlation coefficient

$X$  = trace element A value, ppm

$Y$  = trace element B value, ppm

$N$  = number of samples

$\bar{X}$  = arithmetic mean A

$\bar{Y}$  = arithmetic mean B

$\sigma_x$  = standard deviation A

$\sigma_y$  = standard deviation B

The correlation is valid only for relationships that are close to linear in populations which are symmetrically distributed. The significance of a correlation coefficient is roughly:

0.00-0.20—random relationship, little or no predictive value

0.20-0.40—slight relationship, suggestive of group prediction, of limited or uncertain value

0.40-0.60—moderate relationship, useful for group predictions; geologically important where correlation is greater than 0.50 if causal relationship is known

0.60-0.80—substantially useful for group prediction and some individual predictions

0.80-1.00—highly significant relationship with definite predictive value in individual applications

**floating mean** — The value for any given point on a trend surface determined by averaging the surrounding points with reference to a second (quadratic) or third order (cubic) equation.

**geochemical anomaly** — Any deviation of trace element content in soil above the threshold for that element in soils over barren bedrock.

**histogram** — A bar chart illustrating frequency distribution of any data, e.g., trace-element abundance by logarithmic or arithmetic increments.

**normal probability curve** — a symmetrical, bell-shaped curve which characterizes the distribution of abundance of some homogeneous trace element populations in soils and the analytical error of their determination.

$$y = 0.3989e^{-x^2/2}$$

**relative standard deviation (also coefficient of variation or percent variance)** — The standard deviation expressed as percentage of the arithmetic mean.

$$V = \frac{S}{\bar{X}} \times 100$$

**residual** — The difference between the station value of the element in ppm and the floating mean. It can be either negative or positive.

**standard deviation** — A measure of the amount of scatter around the arithmetic mean.

$$\sigma_x = \sqrt{\frac{\sum (X - \bar{X})^2}{N-1}}$$

$\sigma_x$  = standard deviation

$N$  = number of samples

$X$  = metal content, ppm

$\bar{X}$  = arithmetic mean

**“t” test (also Student “t” test for significance)** — A test for finding the number of chances in a hundred that two arithmetic means are from different populations rather than from chance sampling of one homogeneous population. The formula for this test is as follows (Simpson, Roe, and Lewontin, 1960, p. 422):

$$\bar{X}_1 - \bar{X}_2 \sqrt{\frac{N_1 N_2}{N_1 + N_2}}$$

t =

$$\sqrt{\frac{(N_1 - 1) \sigma_1^2 + (N_2 - 1) \sigma_2^2}{N_1 + N_2 - 2}}$$

$\bar{X}_1$  = arithmetic mean, population A

$\bar{X}_2$  = arithmetic mean, population B

$N_1$  = number of samples, population A

$N_2$  = number of samples, population B

$\sigma_1$  = standard deviation, population A

$\sigma_2$  = standard deviation, population B

The "t" test can also be applied in different form to test the significance of a correlation coefficient.

$$t = \frac{\sqrt{N-2}}{\sqrt{1-r^2}}$$

**threshold** — Upper limit of range of background and the lower limit of a geochemical anomaly. In a normally distributed population it is considered as at least two standard deviations above the mean so that only one sample in 40 would be above this value as part of a normal background population; two and a half standard deviations, one in 160 would be above this value; and only one in 739 samples would be above three standard deviations as part of a normally distributed background. If the population is skewed (and probably composite) the upper 2.5 percent of the data is used as threshold or the second break (flattest part) of the cumulative probability curve.

**trend surface** — A three dimensional mathematical surface illustrating amounts and distribution of trace elements. The surface is defined by various equations that are used for best adapting average trace elements values and minimizing background interference and analytical fluctuations. The equations of different degree of order follow:

Surface	Dependent variable	Linear component	Quadratic component	Cubic component
First-degree		$Z = A + Bx + Cy$		
Second-degree			$Z = A + Bx + Cy + Dx^2 + Exy + Fy^2$	
Third degree				$Z = A + Bx + Cy + Dx^2 + Exy + Fy^2 + Gx^3 + Hx^2y + Ixy^2 + Jy^3$

x and y=coordinates representing planar position

Z = calculated metal content at coordinates x and y

A through J = equation coefficient

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